CHEMICAL VAPOR DEPOSITION AND PROPERTIES OF AMORPHOUS ALUMINUM OXIDE FILMS

ROY G. GORDON, KEITH KRAMER AND XINYE LIU
Department of Chemistry, Harvard University, Cambridge, MA 02138

ABSTRACT

Films of amorphous aluminum oxide were deposited from vaporized alkylaluminum alkoxide compounds and oxygen. For example, a gaseous mixture of triethyldialuminum tri-*sec*-butoxide vapor and dry air deposits amorphous aluminum oxide films on substrates heated to temperatures around 400 °C. Transparent, smooth, adherent films of aluminum oxide were formed on silicon, glass and metal substrates. The new precursors display a number of advantages over previously used sources for aluminum oxide. They are non-pyrophoric, low-viscosity, low-cost liquids. High deposition rates, over 0.2 μm/min, were observed. The coatings have high purity, high electrical resistivity and high transparency to light. They are excellent barriers to diffusion of water and of ions, such as sodium. These films are useful in optical coatings, as wear-resistant hard coatings, and as diffusion barriers that protect flat panel displays, computer microcircuits, solar cells and metals from corrosion and degradation by impurities.

SOME APPLICATIONS OF TRANSPARENT AMORPHOUS ALUMINUM OXIDE

Aluminum oxide is an electrical insulator and is transparent to light over a wide range of wavelengths. It is a strong, hard material, with a high melting point and high thermal conductivity. It resists attack by most chemicals and forms good barriers against diffusion of many materials.

When an alumina film is placed on the surface of a sodium-containing glass, such as common soda-lime glass, it forms an outstanding barrier to diffusion of sodium ions, preventing their entry into devices such as liquid crystal displays, electroluminescent displays, electrochromic windows and solar cells.[1] Alumina also prevents penetration of oxygen and moisture.[2]

Alumina's electrical resistivity and ion barrier properties are exploited in barrier layers in electroluminescent displays and in microelectronics.[3] The hardness of aluminum oxide is used in coatings for machine tools.[4] The chemical inertness of aluminum oxide is useful when it is used as a corrosion-resistant coating on metals, such as steel and aluminum.[5]

SURVEY OF CVD REACTIONS USED FOR ALUMINUM OXIDE FILMS

Production of alumina films has been carried out by a wide variety of methods, including reactive sputtering, evaporation, anodization, sol-gel and chemical vapor deposition (CVD). In this paper, we concentrate on CVD, which can be a very cost-effective process for making high-quality films.

In a CVD process, a precursor vapor reacts on a hot surface to deposit aluminum oxide. Aluminum oxide may be formed by reactions of a wide variety of CVD precursors; however, all the previously reported precursors have serious disadvantages, which we point out in the following survey.

CVD of aluminum oxide has been demonstrated from trialkylaluminum precursors, which have the general formula AlR_3, in which R stands for an organic radical, such as methyl, ethyl, isopropyl, etc. Trimethylaluminum and triethylaluminum are precursors in this class. If vapors of trimethylaluminum are mixed with low concentrations of oxygen near a heated surface, a layer of aluminum oxide is deposited.[6] One disadvantage of this reaction is that the reagents must be mixed immediately over the substrate surface. If the aluminum alkyl and oxygen are mixed more than a few centimeters from the substrate surface, most of the product forms powder or film on the apparatus, and very little film covers the substrate. At atmospheric pressure, turbulent mixing is needed to combine the reagents quickly, and the resulting inhomogeneous gas concentrations of the reactants leads to somewhat non-uniform coating thicknesses. Aluminum alkyls ignite spontaneously in air, so they are a serious fire hazard. Also, CVD processes for forming aluminum oxide films from aluminum alkyls can be disrupted by air leaks into the CVD chamber.

Aluminum 2,4-pentanedionate (also known as aluminum acetylacetonate) is another precursor used for CVD of aluminum oxide. It has the advantage over the aluminum alkyls of not being pyrophoric, and in fact it is completely stable in the presence of air and water at ambient temperatures. Aluminum 2,4-pentanedionate may be vaporized from its melt in a bubbler at temperatures above its melting point of 189 ^{o}C, the vapors mixed with dry oxygen gas, and passed over a heated substrate, in order to deposit films of aluminum oxide.[7] A disadvantage of using aluminum 2,4-pentanedionate is that it decomposes when the material is heated for several hours in a bubbler, so that successive deposition runs do not have the same vapor concentration or deposition rate.

Aluminum isopropoxide has also been used to deposit aluminum oxide films.[8] This material exists in a number of isomeric forms, ranging from dimers to trimers to polymers of various lengths. The rates of interconversion between isomeric forms are slow, often taking days. The vapor pressures of these isomers vary widely. Thus it is very difficult to regulate or predict the vapor pressure of any particular sample of aluminum isopropoxide, and the deposition rate of aluminum oxide is not reproducible. Aluminum 2-ethylhexanoate has been proposed as another source for CVD of aluminum oxide.[9] This solid source material has a very low vapor pressure, which limits the deposition rate to low values.

These aluminum oxide precursors are all solids at room temperature, except for the aluminum alkyls, which are normally liquids. Solid materials are less convenient to handle and move into bubblers, than are liquid precursors. Another advantage of liquid precursors is that they may be vaporized by directly injecting a controlled flow of the liquid into a preheated carrier gas. This direct liquid injection method for vaporization is becoming increasingly widely used in CVD processes, because it allows very reproducible control of the vapor concentration, and minimizes or eliminates premature decomposition of the precursor materials. Thus another disadvantage of the solids, aluminum 2,4-pentanedionate, aluminum isopropoxide and aluminum 2-ethylhexanoate, is that they cannot be vaporized by the direct liquid injection method.

NEW CVD PRECURSORS FOR ALUMINUM OXIDE

We have found that aluminum oxide can be formed from a new group of CVD precursors, the trialkyldialuminum trialkoxides, which avoid the difficulties of the previously known precursors. Examples of these new precursors are triethyldialuminum triisopropoxide and triethyldialuminum tri-*sec*-butoxide. These materials are non-pyrophoric, low-viscosity, non-corrosive, inexpensive liquids. They are easy to vaporize reproducibly without decomposition at temperatures below 200 ^{o}C. Their vapors can be premixed homogeneously with oxygen gas without premature reaction. At substrate temperatures around 400 ^{o}C, these gas mixtures rapidly deposit pure films of amorphous aluminum oxide, with a high conversion efficiency. This substrate temperature is low enough for coating thermally sensitive substrates, such as cut pieces of glass which would lose their flatness if heated to higher temperatures, computer chips which would be damaged by higher temperatures, and metals such as aluminum, which softens and melts at higher temperatures. The reaction by-products are non-corrosive.

Preparation of the new Alkyldialuminum Alkoxide Precursors

Triethyldialuminum tri-*sec*-butoxide may be prepared by mixing equimolar amounts of triethylaluminum and aluminum *sec*-butoxide and heating the mixture to about 180 °C for about 6 hours. The majority of the reaction is described as

$$Et_3Al + Al(sec\text{-}C_4H_9)_3 \; -> \; Et_3Al_2(sec\text{-}C_4H_9)_3$$

By carbon-13 NMR analysis, the resulting reaction product was found to be a mixture containing about 51 mole per cent triethyldialuminum tri-*sec*-butoxide along with smaller amounts of diethyldialuminum tetra-*sec*-butoxide (about 20 mole per cent) and tetraethyldialuminum di-*sec*-butoxide (about 29 mole per cent). Cryoscopic molecular weight determinations showed that these compounds are dimeric in cyclohexane solution. We will refer to this mixture by the name of its major component, triethyldialuminum tri-*sec*-butoxide. The triethyldialuminum tri-*sec*-butoxide mixture is a clear, non-viscous liquid, which may be distilled over a temperature range of about 183-186 °C at a pressure of 40 millibars. Because the volatilities and reactivities of these three alkylaluminum alkoxides are similar, the mixed reaction product may be used as a reactant in CVD processes without further separation or purification.

A similar mixture of alkylaluminum alkoxides is formed by mixing triethylaluminum in hexane solution with 1.5 equivalents of anhydrous *sec*-butanol. Ethane gas is immediately evolved, and then the hexane is removed under vacuum and the product heated to about 180 °C for about 6 hours to yield triethyldialuminum tri-*sec*-butoxide, along with smaller amounts of diethyldialuminum tetra-*sec*-butoxide and tetraethyldialuminum di-*sec*-butoxide.

Use of aluminum isopropoxide in place of aluminum *sec*-butoxide gives a similar mixture which is mainly triethyldialuminum tri-isopropoxide, along with smaller amounts of tetraethyldialuminum di-isopropoxide and diethyldialuminum tetra-isopropoxide. If freshly distilled aluminum isopropoxide is used, fairly complete reaction can be expected. If the aluminum isopropoxide is a commercial solid, or has aged since it has been distilled, then prolonged heating may be required in order to bring the polymeric solid into solution. Analogous reactions were found in which trimethylaluminum was used in place of triethylaluminum.

These liquid precursors all appeared to be non-pyrophoric by the methods published by the United States Department of Transportation. One test calls for placing about 5 milliliters of the liquid or solution on an non-flammable porous solid, and observing that no spontaneous combustion occurs. Another test involves dropping 0.5 milliliters of the liquid or solution on a Whatman No. 3 filter paper, and observing that no flame or charring of the paper occurs.

Experimental Procedure for the CVD Reactions

The liquid precursor mixture was held in a gas-tight syringe, and pumped at a controlled rate with a syringe pump into capillary tubing. The vapor of the liquid precursor was formed by nebulization into a nitrogen carrier gas preheated to about 160 °C. The nebulization was carried out either pneumatically or ultrasonically. Oxygen gas (1 to 10% of the nitrogen flow rate) was added to the vapor mixture downstream from the nebulizer. The vapor mixture then flowed through about 20 cm of tubing heated to 160 °C, so that the gas mixture became homogeneous prior to entering the gas distributors in the CVD equipment. The apparatus spread the vapor mixture of the reactants over a heated substrate on which the aluminum oxide deposits.

The CVD process was carried out at normal atmospheric pressure in two types of equipment. Initial tests were carried out in a static reactor in which the substrate rested on a nickel plate heated from below. A schematic cross section of this apparatus is shown in Figure 1. Substrate temperatures were calibrated by cementing a fine thermocouple to the top of the substrate.

Another nickel plate, suspended 6 mm above the surface of the substrate, formed the upper surface of the rectangular path in which the gas mixture flowed. The upper plate is maintained at a temperature lower than that of the substrate. A gas plenum with small holes distributed the gas uniformly across the 10 cm width of the substrate. Substrates of glass, silicon, stainless steel and aluminum were used.

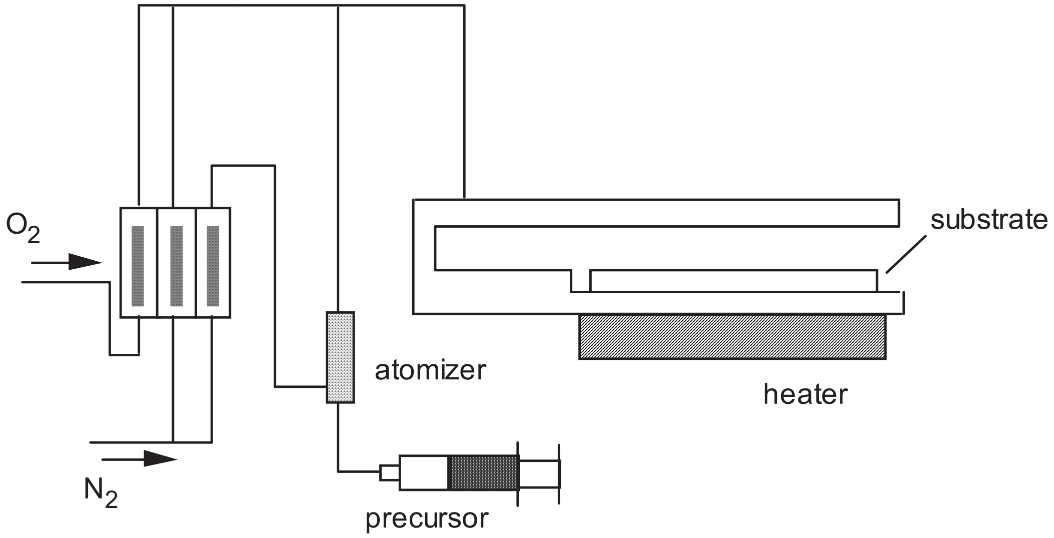

Figure 1. Schematic cross section of the static CVD reactor.

Samples made in this system have a uniform thickness in the direction across the gas flow. However, along the direction of the gas flow, the thickness is not uniform, but instead has a profile with a maximum. At the beginning of the flow, the gas is being heated by the substrate, reactions in the gas phase are just beginning, and the deposition rate is low. As the gas moves downstream across the surface of the substrate, the deposition rate increases to a broad maximum as the reaction reaches steady state. Further downstream, as the reactants are depleted, the deposition rate decreases. The position of the maximum thickness on the substrate increases with the gas flow rate and deceases with increasing substrate temperature.

A second CVD system was based on a furnace with a moving platform, made by BTU International (North Billerica, Massachusetts). The gas mixture was distributed uniformly across the 10 cm width of the substrates. The gas flow divided into equal parts flowing upstream and downstream, with respect to the direction in which the substrate moves. A schematic cross section of this apparatus is shown in Figure 2. The distance that the gas flowed in either direction was 7 cm, until it reached one of the two exhaust slots. In this equipment the samples were carried through the deposition zone at a constant speed. In this way coatings of very uniform thickness were produced, because each part of the sample surface moved through the whole non-uniform profile of deposition rates.

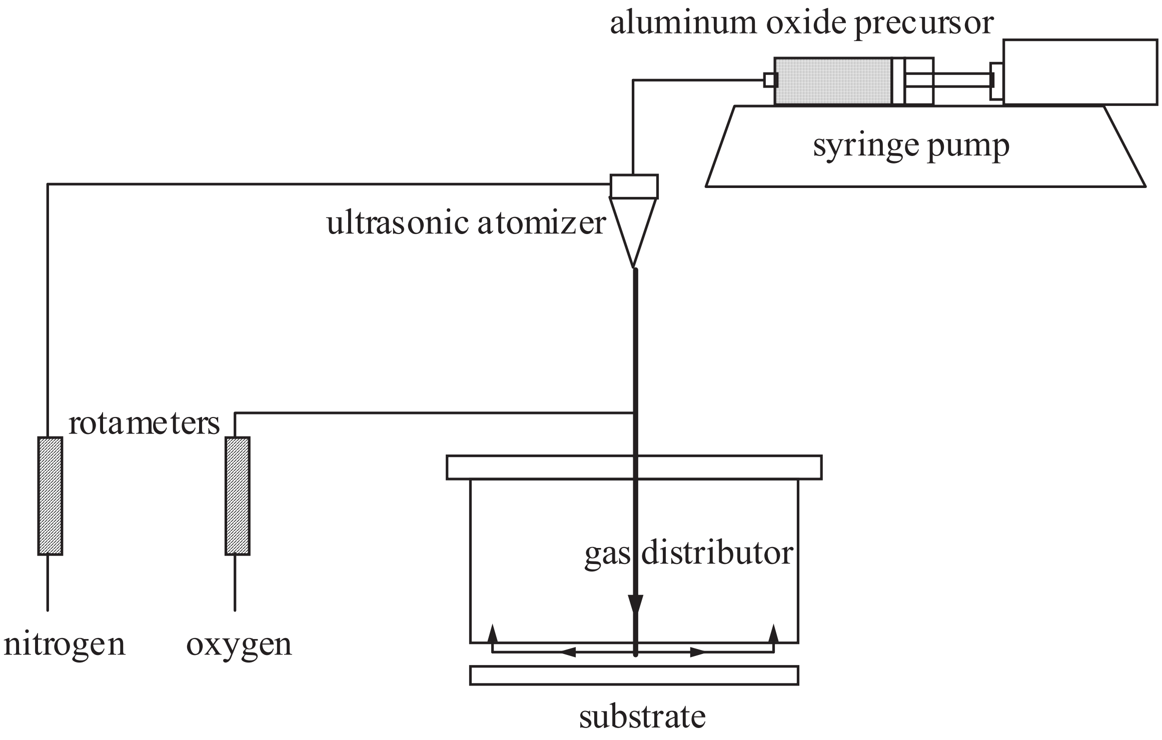

Figure 2. Schematic cross section of the CVD system with a moving substrate.

CVD Experiments

Prior to the deposition and while the glass plate was heating up, dry nitrogen passed through the CVD chamber. Triethyldialuminum tri-*sec*-butoxide was vaporized by pumping the liquid at a rate of 0.1 milliliters per minute into a flow of 8 liters per minute of dry nitrogen gas preheated to a temperature of 160 ^{o}C. A separate gas mixture was formed by the flow of 1 liter per minute of dry oxygen and 2 liters per minute of dry nitrogen. These two vapor mixtures were combined at a tee joint, from which they flowed through a 20 cm length of tubing, into the entrance to the static CVD reactor. The substrate temperature was 400 ^{o}C, while the top plate of the CVD chamber was at about 250 ^{o}C. The flows of triethyldialuminum tri-*sec*-butoxide and oxygen went through the chamber for one minute, during which a layer of aluminum oxide was deposited.

On the surface of the glass plate there was a transparent coating of aluminum oxide with a maximum thickness of about 150 nanometers, as measured by ellipsometry. The deposition efficiency (per cent of the aluminum in the precursor converted to film) is about 30 %.

Similar results were obtained with triethyldialuminum tri-isopropoxide in place of the triethyldialuminum tri-*sec*-butoxide.

CVD experiments were carried out with glass substrates moving at a speed of 5 cm/minute in the BTU furnace. The gas flows and compositions were the same as in the static experiments. Films of very uniform thickness equal to 150 nm were deposited on the glass substrates.

PROPERTIES OF THE ALUMINUM OXIDE FILMS

The chemical compositions of some of the films were measured by Rutherford Backscattering Spectroscopy (RBS), Forward Recoil Spectroscopy (FRS) and by X-ray Photoelectron Spectroscopy (XPS). RBS and XPS detected only aluminum and oxygen in the films. Carbon was not detected by XPS, showing that its concentration is less than about 0.1 atomic per cent.

A film about 1 micron thick was deposited on silicon in the static reactor. Its structure was amorphous by X-ray diffraction, and featureless by SEM.

The films had a refractive index of about 1.6 ± 0.01. The absorption of visible light by a film 1.4 µm thick was less than 0.1 per cent over the wavelength range 500 nm to 800 nm. This same film had 1.3 % optical absorption between the wavelengths of 400 nm and 500 nm.

The dielectric constant was measured by depositing films about 70-170 nm thick on highly doped silicon as a bottom electrode. Top electrodes of platinum were formed by painting areas with an organic platinum solution ("Platinum Bright", A. D. Mackay, Inc., New York) and firing in air at a temperature of 500 ^oC to remove the organic components. Capacitance values of 0.06 to 0.25 $\mu f/cm^2$ were measured with a Boonton Capacitance Meter. Values of the dielectric constant of about 6 to 8 were found. Resistance values of about 10^{12} ohm-cm were measured.

A density equal to 82% of crystalline sapphire was measured by the use of small-angle X-ray reflection, for a film 50 nm thick.

CONCLUSIONS

Aluminum oxide films combine high hardness, transparency, electrical resistivity and chemical durability. Widespread applications of these films have been hindered by lack of satisfactory CVD precursors for their chemical vapor deposition. Previously used CVD processes used precursors that are unsafe (pyrophoric), or inconvenient to handle and vaporize (solids). We presented in this paper a new class of precursors, the trialkyldialuminum trialkoxides, which overcome these difficulties. They are non-pyrophoric liquids with low viscosity, and are easy to vaporize reproducibly and without decomposition. They are inexpensive to manufacture. They deposit smooth, hard, dense and highly transparent aluminum oxide films by CVD at moderate substrate temperatures (around 400 ^oC) and high deposition rates. The films show strong adhesion to a variety of substrates, including glass, silicon and metals. Highly uniform thicknesses were obtained in a simple, cost-effective belt furnace operating at atmospheric pressure. Stoichiometric, pure aluminum oxide was obtained, with an amorphous structure.

ACKNOWLEDGMENTS

This work was supported in part by the U. S. National Science Foundation, and the National Renewable Energy Laboratory under a subcontract from the U. S. Department of Energy.

REFERENCES

---

[1] N. C. Tombs, H. A. Wegener, R. Newman, B. T. Kenney and A. J. Coppola, Proc. IEEE 54, 87 (1966).

[2] P. C. Munro and H. W. Thompson, Jr., J. Electrochem. Soc. **122**, 127 (1975).

[3] T. Kawabe, M. Fuyama and S. Narshige, J. Electrochem. Soc. **138**, 2744 (1991).

[4] B. Lux, C. Colombier and H. Altena, Thin Solid Films **138**, 49 (1986); J. N. Lindstrom and R. T. Johannesson, J. Electrochem. Soc. **123**, 555 (1976).

[5] H. D. van Corbach, V. A. C. Haanappel, T. Fransen and P. J. Gellings, in *Ceramic Films and Coatings*, edited by W. E. Lee (The Institute of Materials, London, 1995), p. 41.

[6] K. M. Gustin and R. G. Gordon, J. Electronic Materials, **17**, 509-517 (1988).

[7] R. G. Gordon, U. S. Patent No. 4 187 336 (5 February 1980).

[8] J. A. Aboaf, J. Electrochem. Soc., **114**, 948-952 (1967).

[9] T. Maruyama and T. Nakai, Appl. Phys. Lett., **58**, 2079-2080 (1991).